

Interfacial Spin Chemistry in Low Symmetry Environments Computational EPR Investigations

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A number of important catalytic processes occur with participation of paramagnetic reactants or are catalysed by open-shell centres, created intentionally on surfaces by various chemical means. Radical species are common intermediates of those reactions, while transition metal ions with the multiplicity of their valence and spin states constitute the active sites. Electron transfer from ligand to metal or from metal to ligand, spin pairing and spin converting processes accompanying the coordination of reactants may drastically alter magnetic states and reactivity of the transition metals, giving rise to electron or spin transfer catalysis. For microporous materials the reactivity may be additionally modified by supramolecular interactions with the nearest surrounding, giving rise to molecular confinement phenomena. In this context, the interfacial coordination chemistry of nitrosyl and carbonyl complexes of transition metal ions in zeolites is particularly distinguished by dramatic changes in the electron and spin states induced by ligation of the CO and NO molecules. Speciation of the resultant cage complexes and their low symmetry give rise to complicated multi-component powder EPR spectra. The overlapped and partially resolved signals severely restrain the recognition of individual EPR features and determination of the spin Hamiltonian parameters. Thus level of sophistication used for the analysis depends critically on quality of the spectra and the ability of their correct reproduction by simulation. As a result, a great deal of important molecular information about the investigated system is only available with the help of advanced computer analysis supported by quantum chemical calculations.

In the computational EPR approach we combine a hybrid genetic algorithm for robust and efficient optimization of complex EPR spectra, with the density functional theory (DFT) calculations of magnetic parameters. Owing to recent progress in the relativistic DFT methods nearly quantitative reproduction of g and A tensors is possible at reasonable computing costs. Available experimental EPR parameters may be therefore directly compared with the corresponding calculated values, providing a quantitative connection between the molecular structure of investigated paramagnets and their spectroscopic fingerprints. This approach was used for guiding the interpretation of changes in the electron and spin states taking place during the interaction of small molecules with surface complexes of transition metals of various electron configurations. Selected examples demonstrate potential of the computational EPR approach in enhancing the interpretation of EPR data of large non-molecular transition metal containing systems.

ACKNOWLEDGMENTS This work has been supported by the Committee for Scientific Research of Poland, KBN, project number 3 T09A 147 26. The calculations have been carried out with the computer facilities of CYFRONET–AGH, the Academic Computing Center, under grant number KBN/SGI2800/UJ/018/2002.